A Molecular-orbital Calculation of Chemically-interacting Systems. Interaction between Two Radicals. Self-reaction of Peroxyl Radicals

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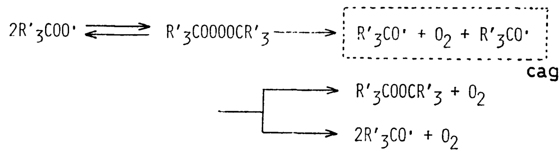
The path of the termination reaction of peroxyl radicals (self-reaction) was studied by means of a perturbational method and its reaction mechanism was elucidated theoretically. It was ascertained from this calculation that the self-reaction of tertiary alkylperoxyl radicals yielding a tetroxide does not have a four-centered transition state with four oxygen atoms of the two peroxyl radicals participating, but has a two-centered transition state with only the terminal oxygen atoms. The self-reaction of primary or secondary alkylperoxyl radicals is found to have a six-centered transition state. The self-reaction of acylperoxyl radicals is also shown to have a six-centered transition state. The mechanism of these self-reactions is clarified in terms of the mode of the particular orbital interaction.

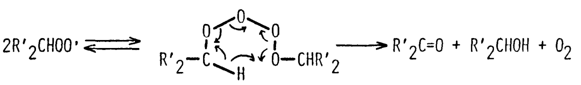
One of the termination reactions of autoxidation is the reaction wherein two peroxyl radicals are converted into non-radical products (self-reaction). Such self-reactions of peroxyl radicals have been studied and various kinds of products have been reported.[1] When a peroxyl radical is represented by ROO·, the products of the self-reaction can be shown to be a function of R. This is displayed in Table 1. When R is a *t*-alkyl group (T) or an acyl group (A), the products of the self-reaction are a peroxide and an oxygen molecule (self-reaction T or A). When R is a *p*-alkyl group (P) or an *s*-alkyl group (S), the products are a carbonyl, an alcohol, and an oxygen molecule (self-reaction SP).

The mechanism involved in these self-reactions has received considerable attention in the last few years because of the fundamental importance of these reactions to a complete understanding of autoxidation. For self-reaction T, the overall process can be represented as follows:[1]



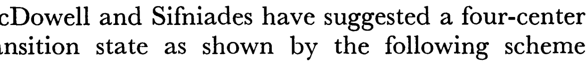
Scheme 1. (for self-reaction T).

This scheme is generally accepted and Bartlett and Guaraldi[2] have provided convincing evidence for the existence of the tetroxide by direct monitoring, using ESR, the concentration of the *t*-butylperoxyl radical, which is present in equilibrium with the tetroxide at very low temperature. Regarding self-reaction SP, its exact mechanism is not yet clear. In this reaction, the carbonyl compounds and alcohol are obtained in high yields, whereas no peroxide, which is present for self-reaction T, was detected.[3] In addtion, when the α-hydrogens of the *s*-, or *p*-alkylperoxyl radicals are replaced by deuterium, an isotopic effect on the rate constant of the overall termination process (*i.e.*, $k_t^H/k_t^D = 1.4$) is observed.[4] k_t is the rate constant of the overall termination process. To explain these experimental results, Russell[5] has proposed a unique mechanism for self-reaction SP which involves the intermediacy of a "cyclic" transition state, as is shown in the following figure:



Scheme 2. (for self-reaction SP).

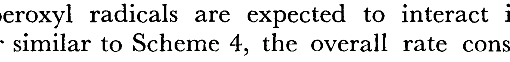
While a mechanism analogous to Scheme 1 with the intermediacy of alkoxyl radicals can be discounted on the basis of experimental results,[3,5] the mechanism of Scheme 2 is supported by most data. However, it has been pointed out that some doubt still remains as to the validity of Russell's mechanism of Scheme 2.[6] Bowman and co-workers[6a] have concluded from thermochemical calculations that, if Scheme 2 is the only viable mechanism for self-reaction SP, the overall activation energy (E_t) should be negative. This is contrary to experimental observations. For example, Howard and Bennett[6b] have found a value of +3 kcal/mol for the E_t of the self-reaction of cyclopentylperoxyl radicals. This discrepancy led Benson propose the following mechanism for self-reaction SP.[6a]



$$2R'_2CHOO\cdot \longrightarrow \boxed{R'_2C{=}\overset{+}{O}{\to}\overset{-}{O} + R'_2\underset{H}{C}OOH}_{\text{cage}} \longrightarrow R'_2C{=}O + R'_2CHOH + O_2$$

Scheme 3. (for self-reaction SP).

However, there is no experimental evidence for the production of a zwitterion and a hydroperoxide from self-reaction SP[1a] and, consequently, this mechanism is not taken into account in this work. Next, for self-reaction A, the mechanism is also controversial. McDowell and Sifniades have suggested a four-centered transition state as shown by the following scheme:[7]



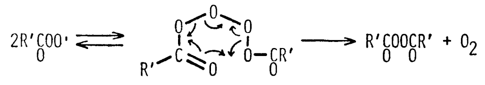
$$2R'\underset{O}{C}OO\cdot \longrightarrow \begin{matrix} & O\cdots\cdots O & \\ R'\underset{O}{C}- & \vdots \quad\quad \vdots & -\underset{O}{C}R' \\ & O\cdots\cdots O & \end{matrix} \longrightarrow R'\underset{O}{C}OO\underset{O}{C}R' + O_2$$

Scheme 4. (for self-reaction A).

However, this scheme appears rather unlikely. While *t*-alkylperoxyl radicals are expected to interact in a manner similar to Scheme 4, the overall rate constant of self-reaction T is much lower than that of self-reaction A, as is shown later in Table 3. Ingold has proposed a six-centered transition state for self-reaction A analogous to Scheme 2,[1b] thus we can write as

TABLE 1. THE PRODUCTS OF SELF-REACTIONS OF PEROXYL RADICALS WITH VARIOUS SUBSTITUENT GROUPS

R	Reaction	Product	Self-reaction
t-Alkyl group (R'_3C-)	$R'_3COO\cdot + R'_3COO\cdot$	$R'_3COOCR'_3 + O_2$	Self-reaction T
s-Alkyl group (R'_2CH-)	$R'_2CHOO\cdot + R'_2CHOO\cdot$	$R'_2CHOH + R'_2C{=}O + O_2$	Self-reaction SP
p-Alkyl group ($R'CH_2$-)	$R'CH_2OO\cdot + R'CH_2OO\cdot$	$R'CH_2OH + R'CH{=}O + O_2$	Self-reaction SP
Acyl group ($R'CO$-)	$\underset{O}{R'C}OO\cdot + \underset{O}{R'C}OO\cdot$	$\underset{O}{R'C}OO\underset{O}{CR'} + O_2$	Self-reaction A



Scheme 5. (for self-reaction A).

Thus, the mechanisms of self-reactions SP and A are still in doubt, although it is accepted that the mechanism of self-reaction T is expressed by Scheme I. Under such circumstances, it is interesting to theoretically study the destruction process of peroxyl radicals. Recently, the ΔW method, which deals with a radical-radical reacting system in terms of the molecular interaction, was developed by the present authors.[8] Some calculations of the ΔW method presented in a previous paper[9] elucidated the difference between recombination and disproportionation mechanisms. In the present work, first, the self-reaction mechanisms will be examined theoretically using the ΔW method. Second, the general aspect of the self-reaction of peroxyl radicals will be explained schematically using the mode of interaction between particular molecular orbitals (MO) of several isolated peroxyl radicals. The reactivity of these radicals can be simply discussed by analyzing the extent of such MO interactions.[10]

Calculation for Assumed Reaction Models

Method of Calculation. In the ΔW method, the wavefunction (Ψ) of a chemically-interacting system consisting of two peroxyl radicals is represented by the sum of various electronic configurations according to the configuration interaction (CI) procedure. Our attention is focused on the reaction system involving singlet spin states because, for triplet spin states, a radical-radical reaction is far from occurring. In this calculation, no electronic configurations for intramolecular excitations are taken into account, as in a previous paper.[9] When the CI secular equation is expanded perturbationally, the total stabilization energy (ΔW) due to the CI mentioned above can be partitioned into the following three terms, Coulomb (E_Q), exchange (E_K) and delocalization (D) terms:

$$\Delta W = E_Q + E_K - D, \tag{1}$$

where E_Q is the classical electrostatic interaction energy between two peroxyl radicals. The exchange energy, E_K, is caused by the overlap between both occupied MO, which are doubly-occupied (DO) or singly-occupied (SO) MO. For the singlet spin state, as well as for the triplet spin state, E_K is found to be repulsive (>0) for systems composed of radicals of usual organic-chemical size.[8] E_K can be further partitioned into four terms, thus

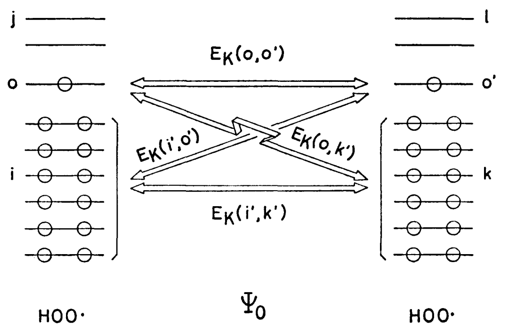


Fig. 1. The adiabatically-interacting configuration (Ψ_0) and the schematic representation of four types of exchange interaction between two hydroperoxyl radical. The lowest and second lowest DOMO's of each HOO·, *i.e.*, the 1s-type ones, are omitted in this figure.

$$E_K = E_K(i', k') + E_K(i', o') + E_K(o, k') + E_K(o, o'). \tag{2}$$

In Fig. 1, the four components of E_K are shown schematically. D is the stabilization energy due to the mixing-in of the charge-transfer configurations with the adiabatically-interacting configuration (Ψ_0). D can be represented by the sum of eight components, thus

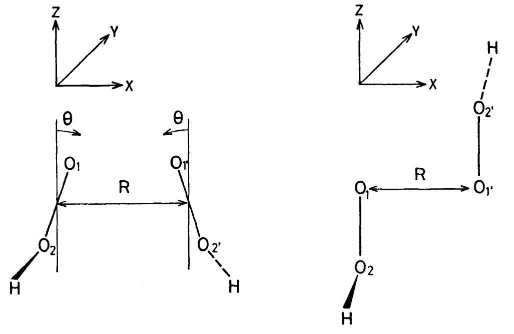
$$\begin{aligned} D &= D(i\to l) + D(k\to j) + D(i\to o') + D(k\to o) \\ &\quad + D(o\to l) + D(o'\to j) + D(o\to o') + D(o'\to o). \end{aligned} \tag{3}$$

A system composed of two hydroperoxyl radicals (2HOO·) is selected as the reaction model for the calculation using the ΔW method. The MO of the hydroperoxyl radical, which are needed to evaluate the CI matrix elements are obtained using the semi-empirical all-valence-electron SCF-UHF method, including overlap integrals.[11] The way of estimating the semi-empirical parameters for evaluating the MO integrals is the same as that used in a previous paper.[12] Since the hydroperoxyl radical has 17 electrons, it has six DOMO, excluding the two lowest 1s-like MO.

The geometry of the assumed reaction models is illustrated in Fig. 2. The geometry of the isolated hydroperoxyl radical comes from the CNDO calculation of Pople and Beveridge[13] and is frozen in the present calculation. In Fig. 2, Model I is a reaction model representing a four-centered reaction path. This model corresponds to Scheme 4. Model II is a two-centered reaction path in which two terminal oxygen atoms (O_1 and $O_{1'}$) are close to each other. Two radical species form the trans conformation. In

TABLE 2. THE CALCULATED INTERACTION ENERGIES FOR THE REACTION OF TWO HYDROPEROXYL RADICALS
The geometrical parameters, R and θ, are those shown in Fig. 2. The smaller value of ΔW indicates higher reactivity. Due to the symmetrical arrangement of the two radicals, $E_K(i', o') = E_K(o, k')$, $D(i \rightarrow l) = D(k \rightarrow j)$, $D(i \rightarrow o') = D(k \rightarrow o)$, $D(o \rightarrow l) = D(o' \rightarrow j)$ and $D(o \rightarrow o') = D(o' \rightarrow o)$.

	Model I					Model II	
	Ia $\theta=0°$		Ib $\theta=+5°$		Ic $\theta=-5°$		
R [Å]	2.4	2.0	2.4	2.0	2.4	2.4	2.0
E_Q [eV]	0.061	0.101	0.088	0.144	0.033	−0.014	0.033
$E_K(i', k')$	0.313	2.239	0.325	2.166	0.444	0.127	0.952
$E_K(i', o')$, $E_K(o, k')$	0.011	0.102	0.023	0.168	0.016	0.020	0.156
$E_K(o, o')$	−0.025	−0.222	−0.034	−0.264	−0.025	−0.003	−0.037
E_K [eV]	0.310	2.221	0.337	2.238	0.451	0.164	1.227
$D(i \rightarrow l)$, $D(k \rightarrow j)$	0.002	0.005	0.002	0.006	0.003	0.002	0.012
$D(i \rightarrow o')$, $D(k \rightarrow o)$	0.008	0.069	0.016	0.120	0.013	0.019	0.155
$D(o \rightarrow l)$, $D(o' \rightarrow j)$	0.000	0.002	0.000	0.001	0.000	0.000	0.001
$D(o \rightarrow o')$, $D(o' \rightarrow o)$	0.034	0.275	0.042	0.324	0.031	0.005	0.050
D [eV]	0.088	0.702	0.120	0.902	0.094	0.052	0.436
ΔW [eV]	0.283	1.620	0.305	1.480	0.390	0.098	0.824



Model I Model II

Fig. 2. Two assumed reaction models employed for the calculation of the interaction energy.

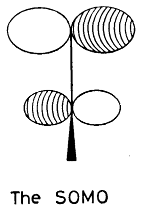
Model I, parameter R is the intermolecular distance between the center of the O_1–O_2 group and that of the $O_{1'}$–$O_{2'}$ group, and θ is defined as the angle between the O_1–O_2 group and the Z-axis. In Model II, R is the distance between the two terminal oxygen atoms (O_1 and O_1'). In both models, the four oxygen atoms (O_1, O_2, O_1', and O_2') are always in the X-Z plane. In Model I, the reacting system belongs to the C_2 point group, whereas, in Model II, to the C_i point group.

Results. The interaction energies (ΔW) for Models I and II are given in Table 2. The ΔW of Model Ia (R=2.4 Å, θ=0°) is compared with that of Model II (R=2.4 Å). This comparison shows that Model II is more favorable than Model Ia for the self-reaction. At R=2.0 Å, the same result is obtained from Table 2. This preference of the self-reaction is thoroughly attributable to the exchange energy term, $E_K(i', k')$ (see Fig. 1). Here, let us examine in more detail the possibility of the four-centered reaction path. In Model I, a variation in θ may bring about a change in ΔW.[14] To see the effect of this angle variation for each energy, two other geometries of Model I are employed. In Model Ib, θ is 5° and, in Model Ic, θ is −5°. Model Ib is a closer approach of two terminal oxygen atoms than Model Ia, whereas Model Ic is a closer approach of the two inner oxygen atoms (O_2 and O_2'). At R=2.4 Å, the approach of the inner oxygen atoms is found to bring about a larger ΔW value (0.390 eV), *i.e.*, destabilization of the system. An analysis of the components of ΔW shows that this destabilization comes primarily from an increase in the exchange energy, E_K. In the three models (Ia, Ib, and Ic), the order of the numerical values of ΔW and its three components are as follows:

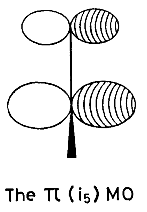
$$\left.\begin{array}{lll} & \text{for } E_Q, & \text{Ib}>\text{Ia}>\text{Ic} \\ & \text{for } E_K, & \text{Ic}>\text{Ib}>\text{Ia} \\ & \text{for } D, & \text{Ib}>\text{Ic}>\text{Ia} \\ \text{and} & \text{for } \Delta W, & \text{Ic}>\text{Ib}>\text{Ia}. \end{array}\right\} R=2.4\,\text{Å}$$

Thus, the superiority of Model Ia is ascribed to the small repulsive terms (E_Q and E_K), in spite of the even smaller attractive term (D). The change in E_Q is very smooth as the intermolecular distance is shortened,[8] whereas E_K and D which are of second order in the MO overlap are shown to increase sharply. Since the rate of growth of D is greater than that of E_K, the approach of two radical species may render Model Ib more favorable than Model Ia. Comparing the ΔW of Model Ia (1.620 eV) with that of Model Ib (1.480 eV) at R=2.0 Å, one really finds this trend. At any rate, Model II is the more favorable pathway of the four assumed reaction models.

The difference in the interaction energies, ΔW, of the models adopted here can be interpreted qualitatively in terms of the shape of the particular MO of the hydroperoxyl radical as follows.[10] The SOMO of the hydroperoxyl radical, which is the seventh MO from the bottom shown in Fig. 1, is a π-type one along the X-axis. It has larger lobes at the terminal oxygen atom than those at the inner atom, as is depicted on the left-hand side of the figure.



The SOMO



The π (i5) MO

The hydroperoxyl radical also has a π-type DOMO (the fifth MO from the bottom in Fig. 1), as is shown on the right-hand side of the figure, which has larger lobes at the inner oxygen atom. In Model Ic ($\theta=-5°$), the approach of the two inner oxygen atoms enlarges the overlapping between these two equivalent DOMO and, at the same time, reduces the overlap between the two SOMO. The increase of the former overlapping makes $E_K(i', k')$ grow large and the reduction of the latter overlapping makes the stabilization terms, $E_K(o, o')$, $D(o\to o')$ and $D(o'\to o)$, become small. The combination of such an increase and reduction results in an unfavorably large ΔW in Model Ic. Since, in Model Ib, the trend of the MO overlapping is opposite (*i.e.*, the SOMO-SOMO overlapping is larger and the DOMO-DOMO overlapping is smaller) to that in Model Ic, the ΔW of the former model becomes favorably small. The even smaller value of ΔW in Model II can be explained in the same way. The favorable results for Model II are attributed to the avoidance of the large overlap between the two DOMO (as shown above) which gives the dominant component of the repulsive term, $E_K(i', k')$. Thus, the loss of the SOMO-SOMO overlapping, which produces three attractive terms, $E_K(o, o')$, $D(o\to o')$, and $D(o'\to o)$, has a negligible influence on the superiority of Model II.

In order to seek the charge-transfer configuration that contributes most to the stabilization of the reaction system, the CI coefficients of Ψ were obtained with respect to Models Ib and II (R=2.0 Å), thus

$$\begin{aligned}\Psi_{\text{Model Ib}} = {} & 0.951\Psi_0 - 0.115\Psi_{o\to o'} - 0.115\Psi_{o'\to o} \\ & + 0.052\Psi_{i_2\to o'} + 0.052\Psi_{k_2\to o} \\ & + 0.046\Psi_{i_5\to o'} + 0.046\Psi_{k_5\to o} + \cdots,\end{aligned} \qquad (4)$$

and

$$\begin{aligned}\Psi_{\text{Model II}} = {} & 0.969\Psi_0 + 0.107\Psi_{i_5\to o'} + 0.107\Psi_{k_5\to o} \\ & - 0.049\Psi_{o\to o'} - 0.049\Psi_{o\to o'} + \cdots.\end{aligned} \qquad (5)$$

In Eqs. 4 and 5, the CI coefficients larger than 0.040 (absolute value) are shown. i_2, i_5, k_2, and k_5 denote the DOMO and the subscripts of i and k are the orbital numbers counted from the lowest DOMO (see Fig. 1). i_5 and k_5 are the π-type MO mentioned above. Equation 4 shows that, except for Ψ_0, the SOMO-SOMO interaction ($\Psi_{o\to o}$ and $\Psi_{o'\to o}$) is the most important in Model Ib, whereas Eq. 5 indicates that the charge transfer (CT) interaction from the π-type MO (i_5 and k_5) to the SOMO (o and o′) is more important than the SOMO-SOMO interaction in Model II.

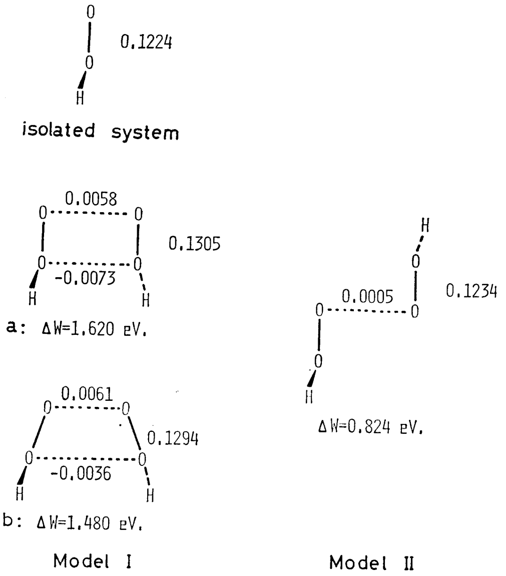


Fig. 3. The change of the atomic bond population by the exchange and CT interactions at R=2.0 Å.

In the course of the reaction, some bonds to be broken are weakened and new bonds begin to form. To see this effect of bond interchange, the atomic bond population[15)] of the chemically-interacting system was calculated using wavefunction Ψ. Models Ia, Ib, and II (R=2.0 Å) were adopted for the calculation and the results are shown in Fig. 3. Judging from the energy results in Table 2, Model Ic is definitely an unfavorable pathway and will not be considered hereinafter. This figure shows that for Models Ia and Ib, a positive intermolecular bond population between the two terminal oxygen atoms (O_1 and $O_{1'}$) appears (0.0058 and 0.0061, respectively). For these two models, however, the intermolecular bond populations between the two inner oxygen atoms (O_2 and $O_{2'}$) are negative (−0.0073 in Model Ia and −0.0036 in Model Ib), which shows that the formation of the new $O_2\cdots O_{2'}$ bond cannot be expressed by them. The O_1–O_2 (or $O_{1'}$–$O_{2'}$) bond population of these two models is larger than that of the isolated HOO·. This can be explained in the following manner. The SOMO of the hydroperoxyl radical is an antibonding π-type orbital, as is sketched above, and therefore the SOMO-SOMO interaction decreases the electron occupancy of the SOMO.[16)] If the reaction proceeds *via* Scheme 4, the O_1–O_2 bond should break in the course of the reaction. However, the present calculated results for the O_1–O_2 bond population together with the negative $O_2\cdots O_{2'}$ population indicate that Scheme 4 is an unfavorable pathway from the standpoint of bond interchange. This is an alternative expression of the improbability of the four-centered pathway. In Model II, a small positive population between the two terminal oxygen atoms appears (0.0005) and that of the O_1–O_2 bond increases only slightly (0.1224→0.1234). The smaller accumulation of the $O_1\cdots O_{1'}$ bond population for Model II than for Model Ib is due to the smaller SOMO-SOMO overlap which is the origin of the intermolecular bonding component.[8,9)] Aside from this comparison of the $O_1\cdots O_{1'}$ bond population, the present results for the atomic bond population show that, in the self-reaction, the two terminal oxygen atoms forms a new $O_1\cdots O_{1'}$ bond, the O_1–O_2 (or $O_{1'}$–$O_{2'}$) bond of the peroxyl radical remaining uncleaved. Also, the self-reaction is found to produce a tetroxide. However, we have here two incompatible results with respect to the superiority of the assumed reaction models. The value of ΔW in Table 2 shows that Model II is the most favorable reaction pathway for the self-reaction, whereas the atomic bond population in Fig. 3 shows that Model Ib is more favorable for the formation of a new $O_1 \cdots O_{1'}$ bond.

Whichever of the pathways corresponding to Model Ib and II the self-reaction takes, the present calculation demonstrates that the reaction path is that for which the two terminal oxygen atoms approach each other and the two inner oxygen atoms do not approach each other as much as the terminal atoms, with the production of a tetroxide resulting. Consequently, the self-reaction process is not that described by Scheme 4. In the present calculation, the system composed of two hydroperoxyl radicals was selected as the reaction model. It is reasonable to consider that a peroxyl radical has an SOMO which is localized mainly over the two oxygen atoms even if the H atom of the hydroperoxyl radical is replaced by any substituent group. Consequently, the results obtained from the present calculation for such a simple system do not appear to be changed markedly upon the replacement of the H atom by a substituent group.

Discussion

In the previous section, the pathways and mechanisms for the self-reactions of peroxyl radicals were investigated using the ΔW method and the self-reaction was shown to give a tetroxide if the terminal oxygen atoms are initially in contact with each other. However, the overall rate constant ($2k_t$) of self-reaction T is quite different from those of self-reactions SP and A, as is shown in Table 3.[1b] The slowness of self-reaction T is primarily due to the fact that the decomposition of the tetroxide intermediate into two alkoxyl radicals and an oxygen molecule requires significant activation energy.[17] Generally, the difference in the rate constants for the three types of self-reactions is ascribed mainly to the differences in the activation energy for tetroxide decomposition.[17b] However, since the difference in the rate constants between self-reaction T and self-reaction SP (or self-reaction A) is much more significant than that expected from the tetroxide decomposition, these may have quite different mechanisms.

The interaction energy, ΔW, is entirely dependent upon the extent of MO overlapping obtained independently for two peroxyl radicals and, therefore, its value can be estimated roughly by analyzing the shape of these MO.[10] Then, even without actually calculating the ΔW, the self-reaction mechanism can be conveniently discussed in terms of the shape of some particular (*frontier*) MO. On this basis, the mechanism of self-reaction SP and self-reaction A will be discussed.

Self-reaction of p- *and* s-*Alkylperoxyl Radicals.* First, the shapes of the MO of a methylperoxyl radical are obtained conveniently by the extended Hückel (EH) MO method[18] and are sketched in Fig. 4(a). In this figure, only the π-type MO are illustrated, because none of the residual MO are as active in causing the important orbital interaction. It was found that the π_3 orbital is the SOMO of the methylperoxyl radical localized over two oxygen atoms. In self-reaction SP, one peroxyl radical abstracts the methyl hydrogen atom of the other and an alcohol is produced. For the geometrical position of two methylperoxyl radicals such that the SOMO-SOMO interaction becomes large, the tetroxide may be produced as was discussed in the previous section. However, for this geometry, the process of hydrogen abstraction cannot be explained. In consideration of this, the CT interaction between the MO of one radical species localized at the C–H bond of a methyl group and the SOMO (π_3) of the other appears to be important in causing reactions other than that producing the tetroxide. In Fig. 4(a), the π_2 orbital is the highest occupied (HO) MO spreading over the C–H bond. When the reacting system has the geometry shown in Fig. 5, the CT interaction from the HOMO (π_2) to the SOMO (π_3) shown in Fig. 5(a and b) is found to contribute to the stabilization of the system. This stabilization corresponds to the higher reactivity of each radical species. This is because, in the reacting regions ($H_4 \cdots O_{2'}$ and $O_1 \cdots O_{1'}$), the lobes of two MO's (π_2 and π_3) overlap in phase. On the other hand, for this geometry, the SOMO-SOMO interaction does not contribute as much because of its nodal properties. Especially, the (HOMO→SOMO) CT interaction shown in Fig. 5(b) is more important than that shown in Fig. 5(a), for these MO have large lobes at the reacting regions ($H_4 \cdots O_{2'}$ and $O_1 \cdots O_{1'}$). The roles of the CT interactions other

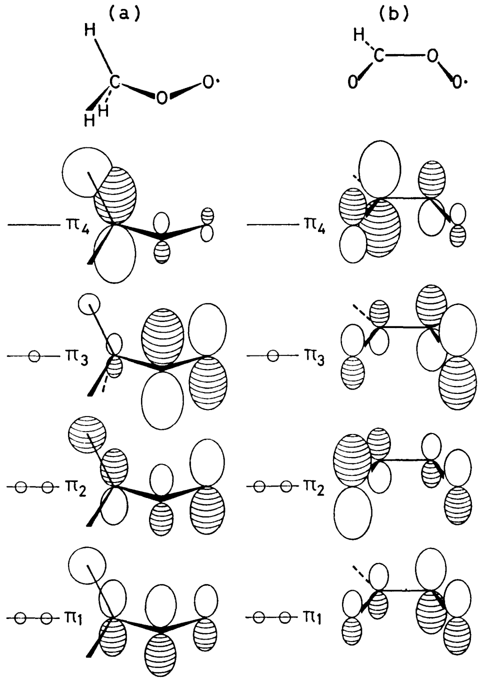


Fig. 4. (a); The schematic representation of the π-type MO's of the methylperoxyl radical. (b); The schematic representation of the π-type MO's of the formylperoxyl radical.
These MO's are obtained by the EH MO method. The geometry of these radicals is obtained from the Pople's standard bond length and bond angle (see Ref. 13).

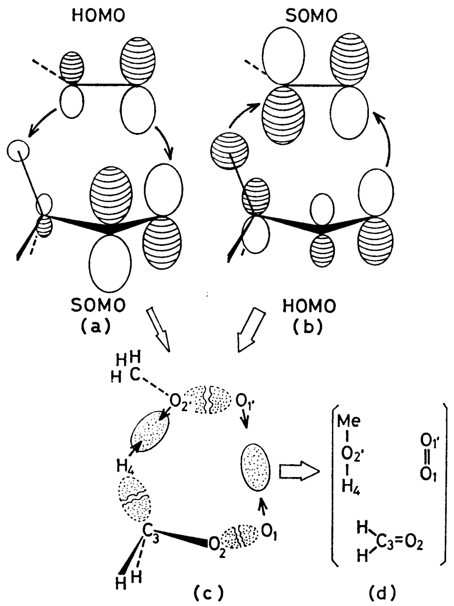


Fig. 5. The CT interaction between the HOMO and SOMO in the self-reaction of the methylperoxyl radicals.

than those depicted in Fig. 5 are minor due to the small value of the corresponding MO overlapping. The CT interaction depicted in Fig. 5(b) will be examined in more detail. This CT interaction contributes to the formation of the new $O_1 \cdots O_1'$ and $H_4 \cdots O_2'$ bonds and the disappearance of the C_3–H_4 and O_1–O_2 bonds through the loss of bonding electrons. Furthermore, the formation of the C_3=O_2 double bond and the disappearance of the O_1'–O_2' bond can also be explained in terms of this CT interaction. Thus, self-reaction SP gives an alcohol, a carbonyl and an oxygen molecule *via* the *six-centered configuration.*

From the above discussion, self-reaction SP can be described as follows. In the initial stage of the reaction, two terminal oxygen atoms (O_1 and O_1' in Fig. 5) approach each other. In this step, if the tetroxide intermediate is not produced, then the reaction system has the six-centered configuration shown in Fig. 5. In this case, the CT interaction between the HOMO spreading over the C_3–H_4 bond and the SOMO is of importance in causing the above-mentioned bond interchange. At this point, the self-reaction produces non-radical products without forming a tetroxide intermediate, as proposed by Russell (see Scheme 2). This picture of the reaction mechanism corresponds to a single-step concerted reaction. However, the bond formation is considered to be concerted, but non-synchronous, as is proposed in many cases of concerted cycloaddition.[14,19] While for cycloaddition (*e.g.*, 1,3-dipolar cycloaddition) two bonds are formed, the bond formation of one of these is, however, advanced with respect to that of the other in the transition state. When self-reaction SP does not have the six-centered configuration, it may readily produce a tetroxide. There is ESR evidence for the formation of a diamagnetic dimer (probably a tetroxide) from two cyclopentylperoxyl radicals.[6b] In short, there are probably two paths for self-reaction SP. One is the path in which a tetroxide is produced, and the other gives an alcohol, a carbonyl and an oxygen molecule. This reaction picture is in agreement with that suggested by Howard and Bennett.[6b] Although these authors gave no detailed discussion of the structure of the transition state in their mechanism, they suggested that in self-reaction SP one pathway giving non-radical products is different from the other which produces a tetroxide. Furthermore, they represented this suggestion schematically using the potential energy-reaction coordinate curve drawn in Fig. 6. When we examine the six-centered configuration of the transition state introduced in this work, it is seen that the present picture of self-reaction SP is in line with their suggestion. According to this picture and the experimental evidence mentioned above, the products and, furthermore, the isotopic effect are easily interpreted. If two peroxyl radicals react in the singlet spin state, the spin-conservation rule requires either that the oxygen molecule evolved in the self-reaction should be formed in an excited singlet spin state or that it should be in a ground triplet state and the carbonyl in an excited triplet state.[1b] Many experiments show that the oxygen molecule is formed in an excited singlet state.[20] Such data is in line with the present picture of the single-step concerted reaction. Thus, it is probable that self-reaction SP has a six-centered transition state as proposed by Russell, although the Russell scheme (Scheme 2) should be somewhat modified to the present picture mentioned above.

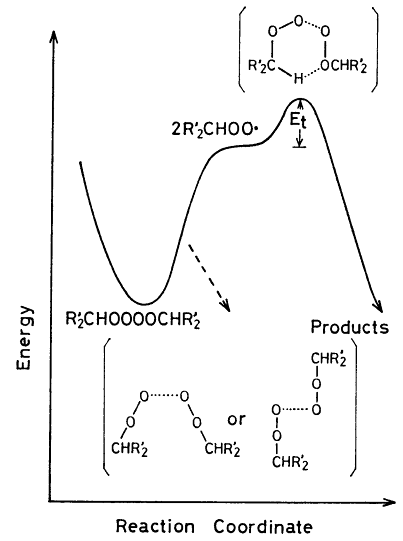


Fig. 6. The potential energy-reaction coordinate curve of the self-reaction SP taken from Ref. 6(b). The six-centered transition state obtained in the present work is additionally depicted and the two-centered path producing a tetroxide is also pictured.

Self-reaction of Acylperoxyl Radicals. The overall rate constant for self-reaction A is much larger than that of self-reaction T, as is shown in Table 3. The acylperoxyl radical has a C=O bond at the α-carbon atom which corresponds to the C–H bond of the *p*- and *s*-alkylperoxyl radicals. For self-reaction A, the possibility of a six-centered transition state of the self-reaction

TABLE 3. THE OVERALL RATE CONSTANTS ($2k_t$) FOR THE SELF-REACTIONS[1b)]

Radical	$2k_t$, $M^{-1}\,s^{-1}$	Self-reaction[a)]
t-Alkylperoxyl	$0.1—60\times10^4$	T
s-Alkylperoxyl	$1—40\times10^6$	SP
p-Alkylperoxyl	$2—8\times10^8$	SP
Acylperoxyl	$10^6—10^{11}$	A

a) The classification of the self-reactions is given in Table 1.

will be examined. To determine the shape of the MO of the acylperoxyl radical, those of a formylperoxyl radical were obtained simply using the EH MO method. In Fig. 4(b), only the π-type MO are depicted according to the same criterion as that for the methylperoxyl radical. From Fig. 4(b), it is found that the π_3 orbital is an SOMO localized appreciably about two oxygen atoms (O–O bond) and that the π_2 orbital is the HOMO spread over the C=O double bond. In Fig. 7 is shown the mode of the mutual CT interaction between the HOMO of one radical species and the SOMO of the other. The CT interactions other than those are not as important for the same reason as the case of the methylperoxyl radical. The (HOMO→SOMO) CT interaction in Fig. 7(a) is more important than that in Fig. 7(b) in the sense that the former interaction is caused by the larger overlap in the reacting regions ($O_2\cdots O_{4'}$ and $O_1\cdots O_{1'}$). Looking at the mode of the (HOMO→SOMO) CT interaction of Fig. 7(a and b), one can reasonably understand the process of bond interchange which is similar to the case of the methylperoxyl radical. The intermolecular $O_1\cdots O_{1'}$ and $O_2\cdots O_{4'}$ bonds are formed and the $O_{2'}$–$C_{3'}$ single bond is converted to the $O_{2'}$=$C_{3'}$ double bond. Furthermore, the O_1–O_2 and $O_{1'}$–$O_{2'}$ bonds disappear and the $C_{3'}$=$O_{4'}$ double bond is converted to the $C_{3'}$–$O_{4'}$ single bond. Thus, it is anticipated that, in order to bring about effective (HOMO→SOMO) CT interactions, self-reaction A has the six-centered configuration giving no tetroxide, but non-radical products (the peroxide and oxygen molecules). This picture of the reaction mechanism also corresponds to a single-step concerted reaction. If self-reaction A proceeds along this reaction path, it leads again to the prediction that self-reaction A gives an oxygen molecule in the excited singlet state. Unfortunately, since the data for the spin state of the oxygen molecule produced in self-reaction A do not yet appear to be available, further experimental verification is desirable. It should be noted that in the approach of the two terminal oxygen atoms, self-reaction A may also give a tetroxide as in the case of self-reaction SP.

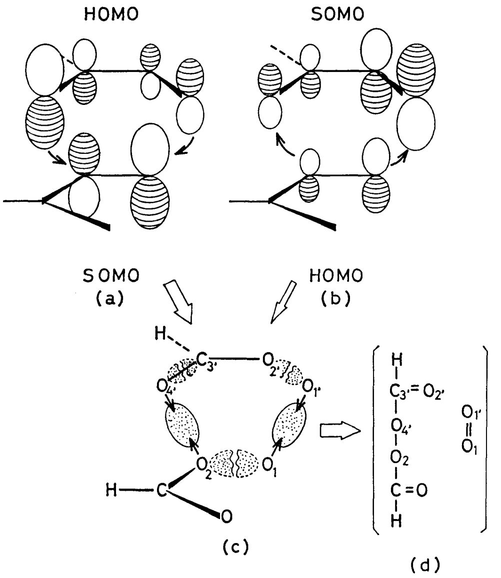


Fig. 7. The CT interaction between the HOMO and SOMO in the self-reaction of the formylperoxyl radicals.

Conclusion

From this work, a discussion based on the ΔW method was made with respect to the self-reaction of peroxyl radicals. First, the interaction energy, ΔW, was calculated using the simplest peroxyl radical (HOO·). One implication derived from this calculation is that, aside from the superiority of either the trapezoid or trans configurations, the two-centered transition state is more probable than the four-centered one. Second, when three types of substituents (*t*-alkyl, *s*- and *p*-alkyl, and acyl) are taken into account, other reaction mechanisms involving them are introduced. In the case of the self-reaction of both *s*- and *p*-alkylperoxyl and acylperoxyl radicals, the termination is a single-step concerted reaction with a six-centered geometrical configuration. In the former self-reaction, a C_α–H bond is ruptured whereas, in the latter self-reaction, a C_α=O double bond is converted into a single C_α–O bond. There, the CT interaction between the HOMO spread over the C–H or the C=O bond of one peroxyl radical and the SOMO of the other is of importance in triggering the bond interchange. However, in the self-reaction, *t*-alkylperoxyl radicals which do not have a C_α–H bond cannot undergo this termination reaction, but produce solely a tetroxide.

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